

1

PROCESS FOR SYNTHESIS OF AMMONIA BORANE FOR BULK HYDROGEN STORAGE

CROSS REFERENCE TO RELATED APPLICATION

This application claims priority from Provisional application No. 61/055,251 filed 4 Apr. 2007, incorporated in its entirety herein by reference.

GOVERNMENT SUPPORT

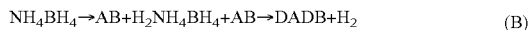
This invention was made with Government support under Contract DE-AC0676RLO-1830 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

FIELD OF THE INVENTION

The present invention relates generally to methods for the synthesis of ammonia borane. More particularly, the invention relates to a new method for the synthesis of ammonia borane in liquid ammonia and an ether-based solvent that provides ammonia borane at a high yield and a high purity.

BACKGROUND OF THE INVENTION

Many research groups around the world are investigating approaches to accelerate the discovery and development of hydrogen storage materials and systems to meet Department of Energy (DOE) 2015 system-based targets. A hydrogen storage system includes all the components required to get hydrogen from a hydrogen storage material and provide it to the end device or operating system, e.g., a fuel cell. System components can include, e.g., storage tanks, heat exchangers, valves, tubing, pumps, and other components. However, weights must be considered before each individual component can be considered as a component within the selected operating system. System target goals have been developed through the FreedomCAR Partnership between DOE and the US Council for Automotive Research (USCAR, www.uscar.org). Ammonia borane (NH_3BH_3), denoted herein as (AB), has a potential to meet established targets for a viable hydrogen storage material and to provide hydrogen for use as an operating fuel. Several processes are described in the literature for synthesizing ammonia borane AB. In the conventional metathesis approaches, synthesis of AB involves two undesired pathways that involve formation of DADB, the ionic dimer of AB, as shown hereafter:



In pathways (A) and (B), NH_4BH_4 decomposes to form AB with loss of H_2 gas. However, as AB is formed, AB can dimerize as in pathway (A) to form DADB or can lose hydrogen and form polymeric polyaminoborane (PAB), a decomposition product. Alternatively, AB can also react with NH_4BH_4 as in pathway (B) to form DADB or PAB. Increasing the AB concentration or temperature increases the likelihood of reactions that form DADB and PAB. In these approaches, DADB is a competing reaction component that can decrease the yield of AB. In an alternative metathesis approach performed in an organic solvent, dilute reactant concentrations were used in an attempt to prevent DADB or PAB formation. However, low yields of AB were obtained. In another approach known in the art, an attempt was made to promote

2

H_2 loss from NH_4BH_4 in NH_3 to form AB by heating (e.g., at 40°C .), but various and multiple reaction products were obtained by heating the NH_3 solution that decreased the yield of AB as well as the purity of the product. In short, current methods are limited by problems including, e.g., dilute reactant concentrations; competing side reactions and products including, e.g., polymeric products (e.g., DADB and PAB); complex product recovery; toxic solvents; low product purity; and low product yields. Accordingly new methods are needed that improve reaction efficiencies and provide greater yields of AB at a greater purity.

TERMS

The following terms are used herein.

The term "liquid ammonia" means anhydrous ammonia in the liquid state; not ammonia water.

The term "sequential" refers to process steps that are performed serially, i.e., one by one, or one after the other.

The term "parallel" refers to process steps that are generally performed together or simultaneously, e.g., by adding one or more required reagents at the same time, or conducting one or more reaction steps simultaneously.

The term "near-quantitative" as used herein means greater than or equal to 99% of the theoretical yield. A quantitative yield means 100% of the theoretical yield for the reaction.

SUMMARY OF THE INVENTION

In one aspect, the invention is a new method for synthesis of ammonia borane. The method includes the steps of: reacting a preselected quantity of a borohydride salt and an ammonium salt in liquid ammonia at a preselected temperature and pressure forming ammonium borohydride; and adding a preselected quantity of an ether-based solvent to ammonium borohydride to form ammonia borane (AB) at a high yield and a high purity. The invention overcomes: need for toxic solvents, dilute reagent conditions, complex product isolation and recovery, competing side reactions and side reaction products, low product yields, and low product purity. Yield of ammonia borane is greater than or equal to about 90%. More particularly, yield of AB is greater than or equal to about 99%. In one embodiment, yield of AB is greater than or equal to 99% by weight with a purity greater than or equal to 99%. The liquid ammonia (NH_3) solvent overcomes unwanted side reactions and maximizes formation of AB. Concentration of the ammonia (NH_3) is greater than or equal to about 10 percent by weight. Ether-based solvents include, but are not limited to, e.g., glyme; diglyme; ether; tetrahydrofuran (THF); and combinations of these solvents. The invention provides concentrations of AB up to about 2.5M currently in the ether-based solvent. Temperatures for conducting the reactions can be varied. In particular, temperatures can range from about -80°C . to about 25°C . More particularly, temperatures can range from about -40°C . to about 25°C . Various ammonia (NH_3) pressures can also be used. Ammonia pressures can be selected in the range from about 1 atmosphere (for low-temperature syntheses) up to about 20 atmospheres at near room temperature synthesis conditions. Preferred synthesis conditions are $0-25^\circ\text{C}$. at 100-300 psia of NH_3 , but conditions are not limited thereto.

In one embodiment, liquid ammonia is not removed.

In one embodiment, a borohydride salt reactant is mixed with an ammonium salt reactant to form borohydride (NH_4BH_4) solid at an elevated temperature (15°C .) under a NH_3 partial pressure of 7.2 atm. that maintains liquid ammonia conditions.